UNIVERSITY OF ZAGREB

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

FKITMCMXIX

POLYMER SCIENCE AND TECHNOLOGY

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Classification of polymerization reactions:

according to:

1. **mechanism of chain growth**
2. **media of polymerization**

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1. Polymerizations
by the mechanism of chain growth

Mechanism of chain growth

RADICAL POLYMERIZATION

STEP BY STEP POLYMERIZATION

Mechanism of chain growth (*type of reaction*)

1. free-radical polymerization

addition polymerization, chain-growth of polymer

I. initiation
II. propagation
III. termination

2. step by step polymerization

condensation polymerization, stepwise growth of polymer

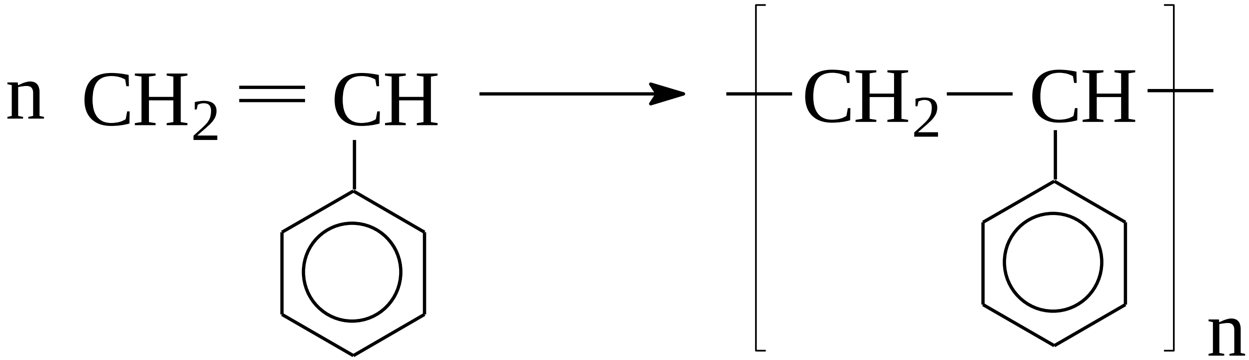
monomer + monomer → dimer
dimer + monomer → trimer
dimer + dimer → tetramer
trimer + monomer → tetramer etc.

1. FREE-RADICAL POLYMERIZATION

$$CH_2 = CH_2 \longrightarrow \left[CH_2 - CH_2 \right]_n$$

ethylene polyethylene

Low density polyethylene is produced by free radical polymerization.



styrene

(vinyl-benzene)

polystyrene

Free-radical polymerization

Three phases:

I. **initiation**
II. **propagation**
III. **termination**

1. Initiation – initiator decomposition

$$I \xrightarrow{k_d} 2R^{\bullet}$$

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet}$$

Primary active species

Initiators: **specific decomposition temperature!**

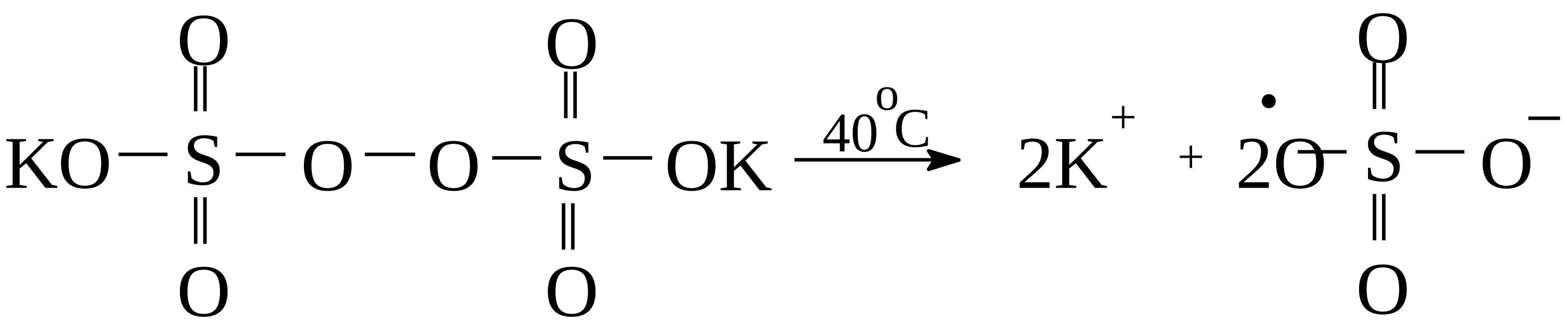
a) inorganic initiators

hydrogen peroxide, H_2O_2 (O-O bond)

$$HO-OH \xrightarrow{60^{o}C} 2\dot{O}H$$

hydroxyl radical

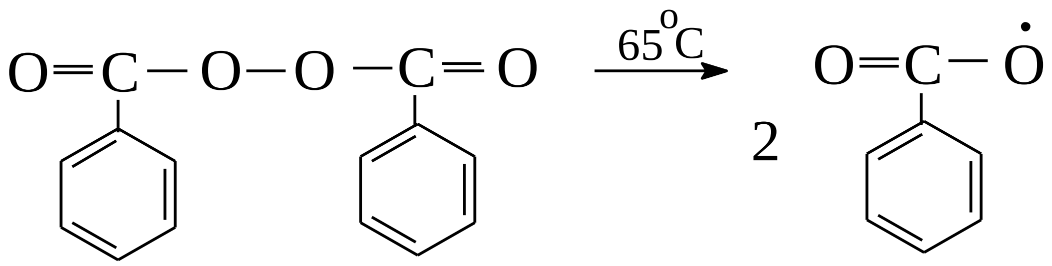
potassium persulfate, $K_2S_2O_8$ (O-O bond)



sulfate anion radical

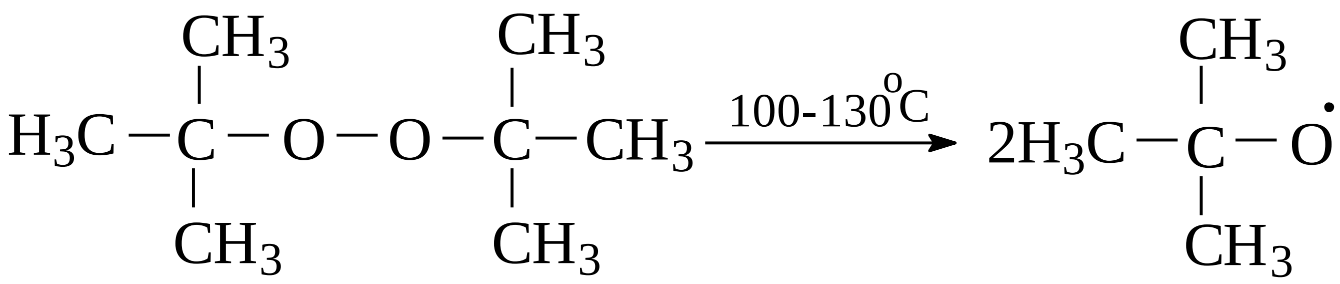
b) Organic peroxides

benzoyl peroxide, DBP (O-O bond)



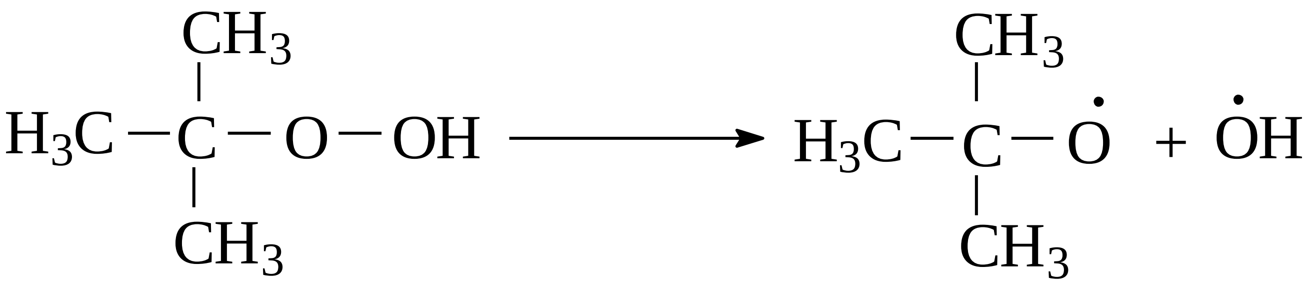
benzoyloxy radical

Di-tert-butyl peroxide (O-O bond)



t-butyloxy radical

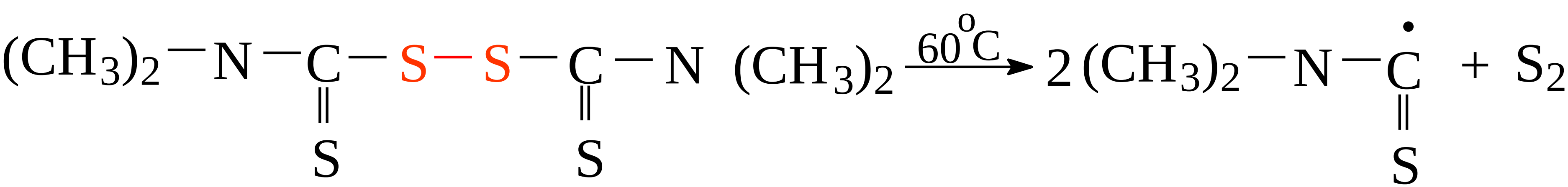
t-butylhydroperoxide (O-O bond)



c) initiators with S-S bond

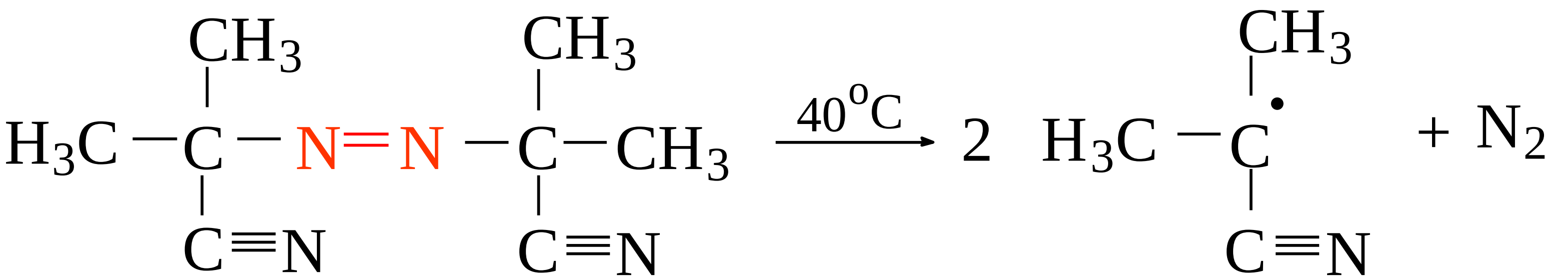
Tetramethylthiuram disulfide , TMTD

- vulcanization



d) Initiators with N-N bond

α,α'-azobisisobutyronitrile, AIBN



2-cyano-2-propyl radical

The example of

free-radical polymerization:

ethylene polymerization

1. Initiation

$$I \longrightarrow 2\dot{R}$$

$$H_2O_2 \longrightarrow 2\dot{O}H$$

decomposition of initiator

$$R\bullet + CH_2 = CH_2 \rightarrow R - CH_2 - \dot{C}H_2$$

$$R\bullet + M \xrightarrow{kp} RM\bullet$$

2. Propagation

$$R-CH_2-\dot{C}H_2 + CH_2 = CH_2 \rightarrow R-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$\mathrm{RM}^{\bullet} + M \xrightarrow{kp} \mathrm{RMM}^{\bullet}$$

3. Termination – the end of polymerization

a) combination

$$\mathrm{RM}_n^{\bullet} + \mathrm{M}_m^{\bullet}\mathrm{R} \xrightarrow{k_{tk}} \mathrm{RM}_n\mathrm{M}_m\mathrm{R}$$

b) disproportionation

$$RM_n^{\bullet} + \overset{\bullet}{M}_m R \xrightarrow{k_{td}} RM_n + RM_m$$

c) chain transfer

$$RM_n^{\bullet} + RH \xrightarrow{k_{tt}} RM_n + R^{\bullet}$$

I- Initiator, $R^{\bullet}$- radical, M - monomer, k_d – constant of dissociation k_i- constant of initiation, k_p- constant of propagation, k_{tk}- constant of transfer with combination, k_{td}- constant of disproportionation, k_{tt}- constant of chain transfer

a) combination

$$RM_n^{\bullet} + M_m^{\bullet}R \xrightarrow{k_{tk}} RM_nM_mR$$

$$R-[CH_2-CH_2-]CH_2-\dot{C}H_2+\dot{C}H_2-CH_2-[CH_2-CH_2-]R \rightarrow$$

$$R-[CH_2-CH_2-]CH_2-CH_2-CH_2-CH_2-[CH_2-CH_2-]R$$

Product: one polymer chain

b) disproportionation

$$RM_n^{\bullet} + \dot{M}_m R \xrightarrow{k_{td}} RM_n + RM_m$$

$$R-[CH_2-CH_2-]CH_2-\dot{C}H_2+\dot{C}H_2-CH_2-[CH_2-CH_2-]R \rightarrow$$

$$R-[CH_2-CH_2-]CH_2-CH_3+CH_2=CH\ -[CH_2-CH_2-]R$$

terminated polymer chain

Double bond can be attacked by radical
- new polymerization starts

Product: two polymer chains

c) chain transfer – transfer of polymerization reaction to „something else" in a recation mixture – *in general, it is not favorable type of termination*

$$R-[CH_2-CH_2-]CH_2-\dot{C}H_2+RH \rightarrow R-[CH_2-CH_2-]CH_2-CH_3+\dot{R}$$

RH may be initiator

solvent

monomer

polymer

Chain transfer with initiator

Initiator forms the first radicals, then attacks monomer and forms further radicals.

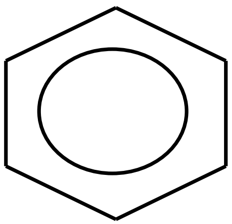
Chain transfer with initiator rarely happens - *the added quantity of initiator is very small (0,1%).*

At the end of polymerization there is no initiator.

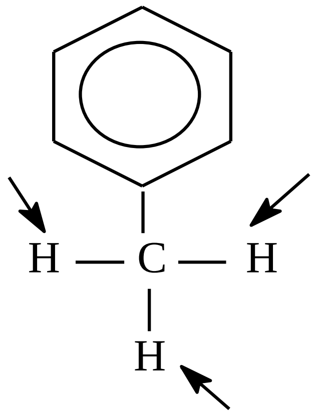
Chain transfer with solvent

Solvent is always present except at polymerization in bulk.

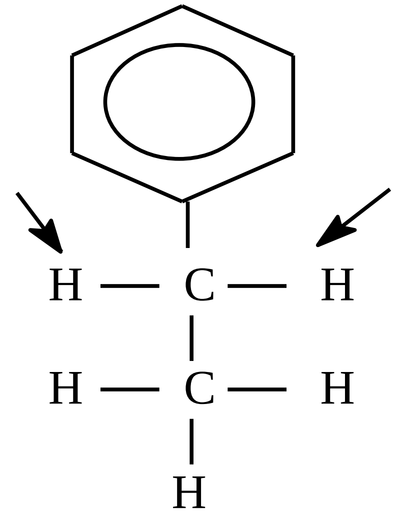
Aldehides and ketones are very good chain transfer solvents because of easy discharge of H-atom.



benzene

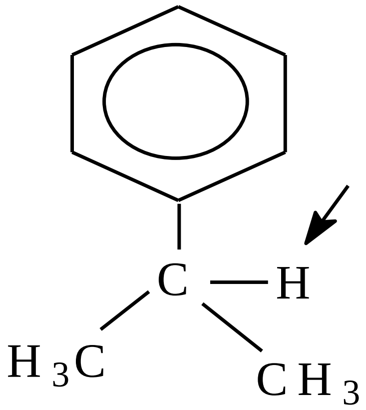


toluene

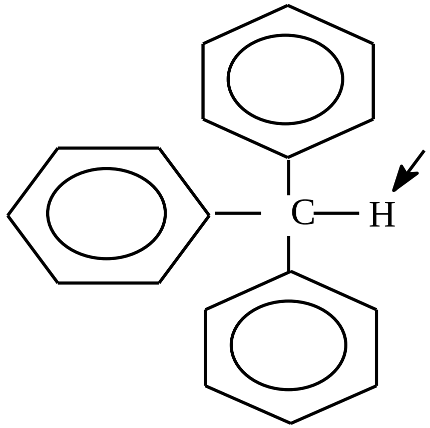


ethylbenzene

better chain transfer



cumene



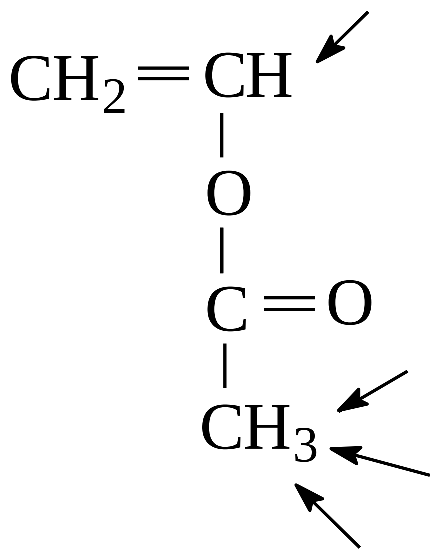
tri phenylmethane

better chain transfer →

Chain transfer with monomer

Chain transfer with monomer rarely happens, because at the and of polymerization there is no monomer any more.

Very reactive monomer is vinyl-acetate

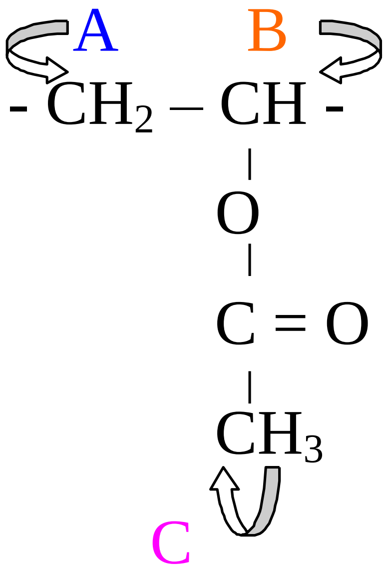


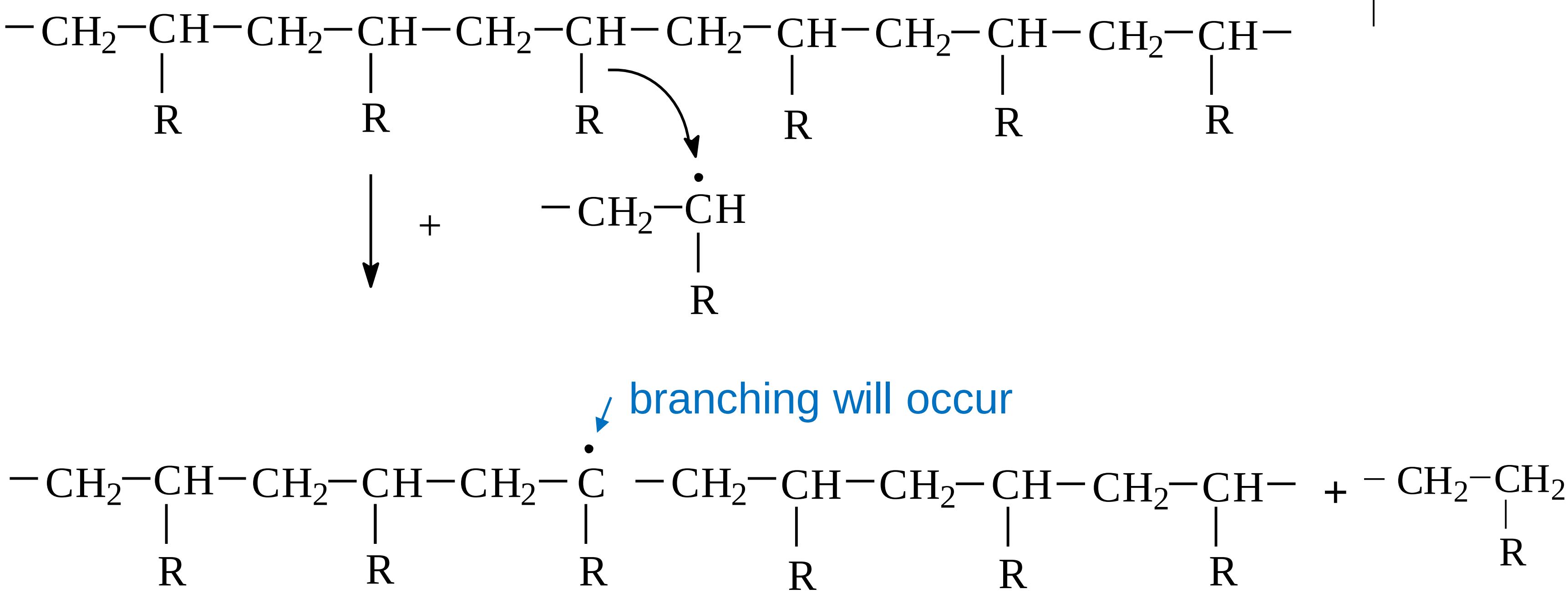
Chain transfer with polymer

Product: branched or crosslinked polymer

It is most common chain transfer, because at the end of polymerization there are only solvent and polymer.

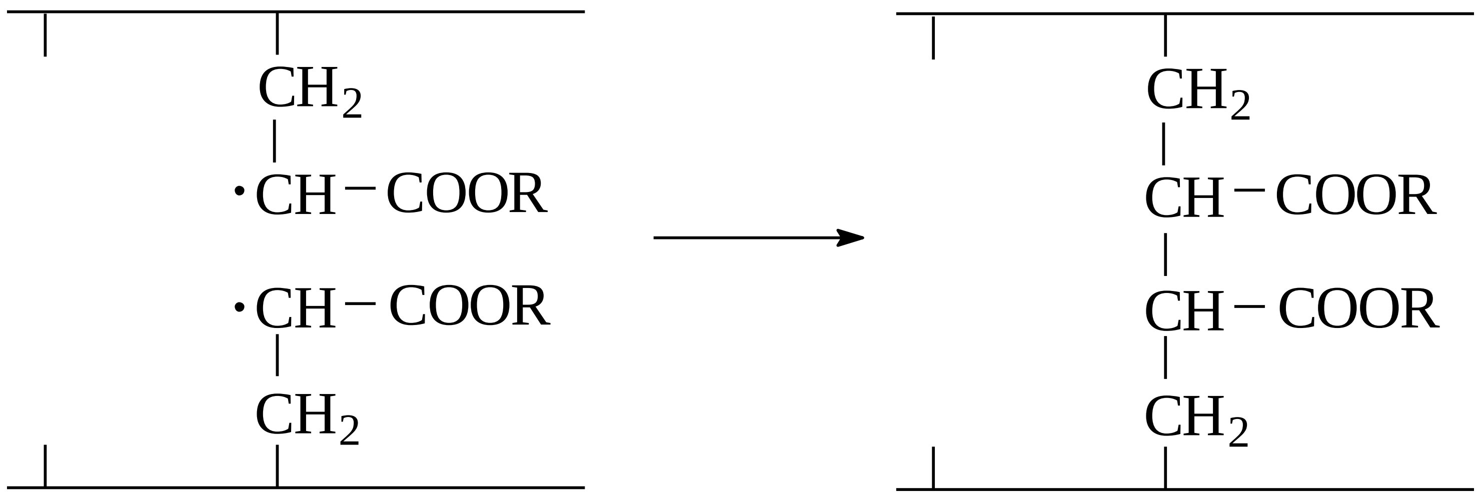
Example: reactivity of poly(vinyl-acetate)




branching will occur

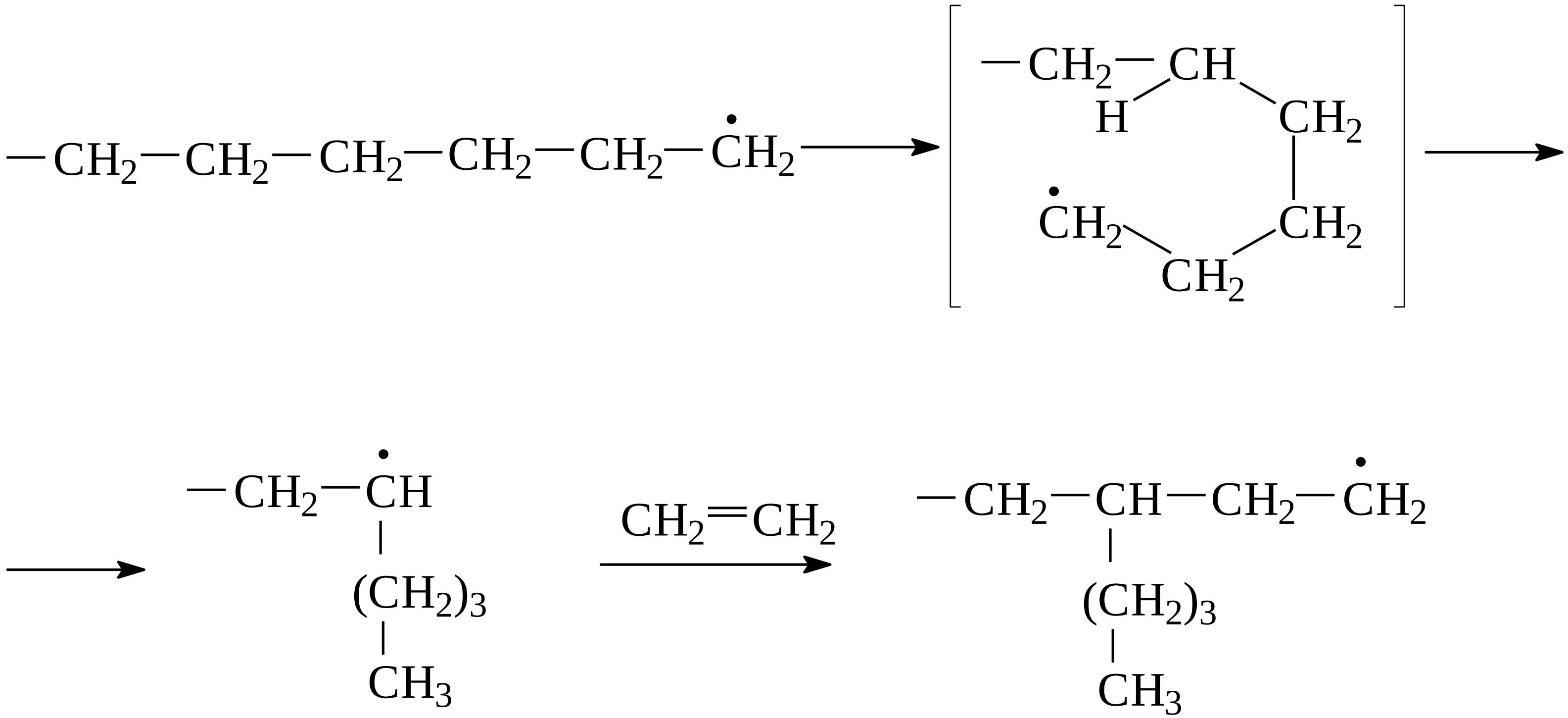
During a free radical polymerization there is always a possibility for polymer branching.

Example: polyacrylate with high constant of chain transfer - the result is crosslinked polymer



- very interesting polyethylene chain transfer:

chain reacts with its own chain – intramolecular bonding



This reaction is called «**backbiting**» - it means "to bite its own tail".

STEP BY STEP POLYMERIZATION *condenzation polymerization*

- the product of the reaction are polymers and „little" molecules (water, ammonia, CO_2 ,HCl, N_2, methanol)
- polymerization in which the polymer's molecular weight increases in a slow, stepwise manner as reaction time increases.

Step by step polymerization

- ***condensation polymerization***
- stepwise growth of polymer

monomer + monomer → dimer
dimer + monomer → trimer
dimer + dimer → tetramer
trimer + monomer → tetramer etc.

The product is **polycondenzate**

Step by step polymerization: 2 types

1. ***Two* different polyfunctional monomers**
   - ***every monomer has only one type of functional group:***

n H_2N-R-NH_2 + n HOOC-R'-COOH →
→ $[HN\text{-}R\text{-}NH\text{-}OC\text{-}R'\text{-}CO]_n$ +n H_2O

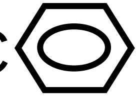
or generally:

n A-A + n B-B → $[A\text{-}A\text{-}B\text{-}B]_n$

HOOC-$(CH_2)_4$COOH + H_2N $(CH_2)_6NH_2$ → -[OC-$(CH_2)_4$-CO-NH-$(CH_2)_6$NH]- + $2H_2O$

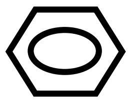
adipic acid	hexamethylene diamine	nylon 6,6 – polyamide - amide group: CONH

Example: polyester (PET), ester group: COO

$n\ HOCH_2CH_2OH$ + n HOOC  COOH $\leftrightarrow$

monomer
ethylene glycol
(EG)

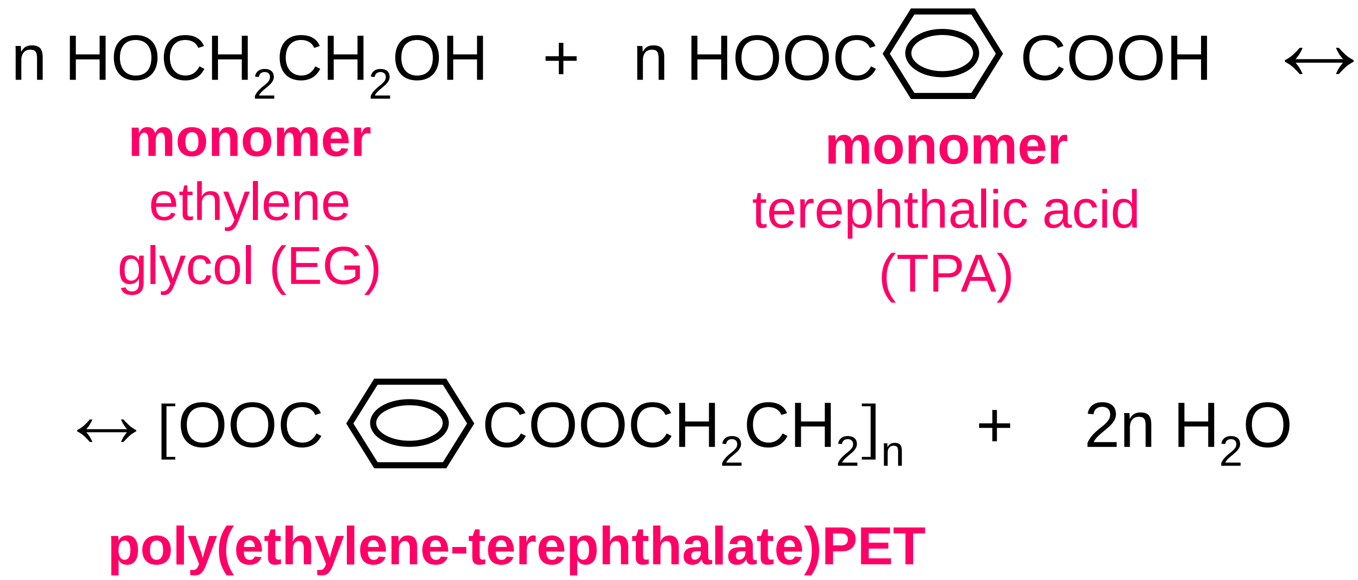
monomer
terephthalic acid
(TPA)

$\leftrightarrow$ [OOC  $COOCH_2CH_2]_n$ + $2n\ H_2O$

poly(ethylene-terephthalate), PET

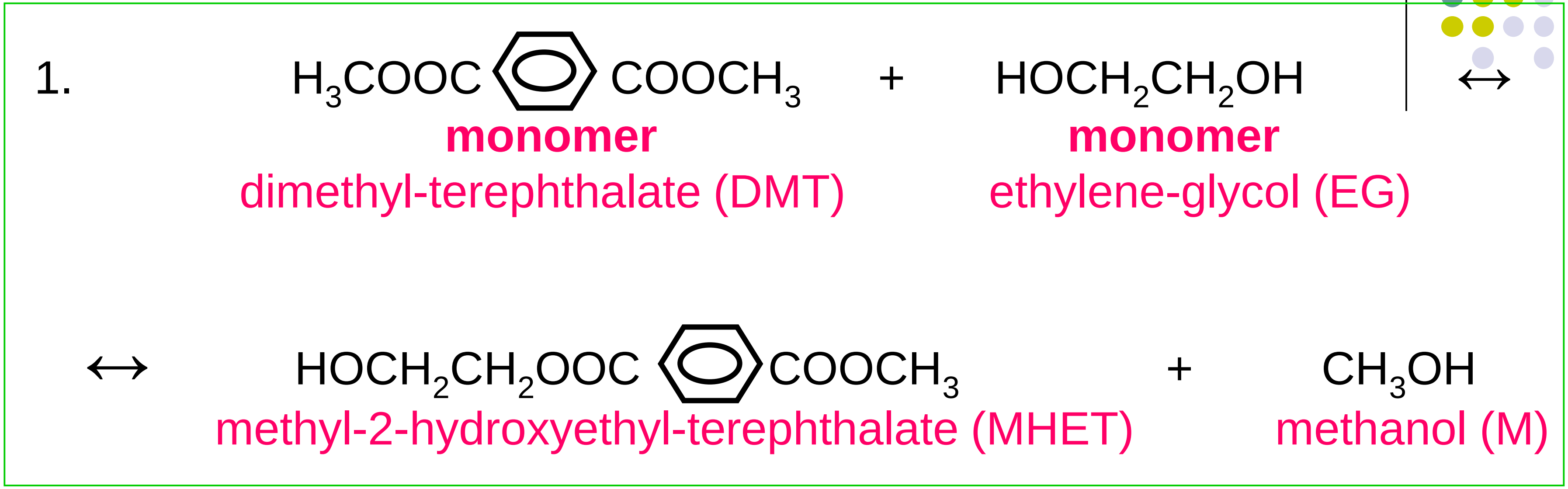
Production of PET

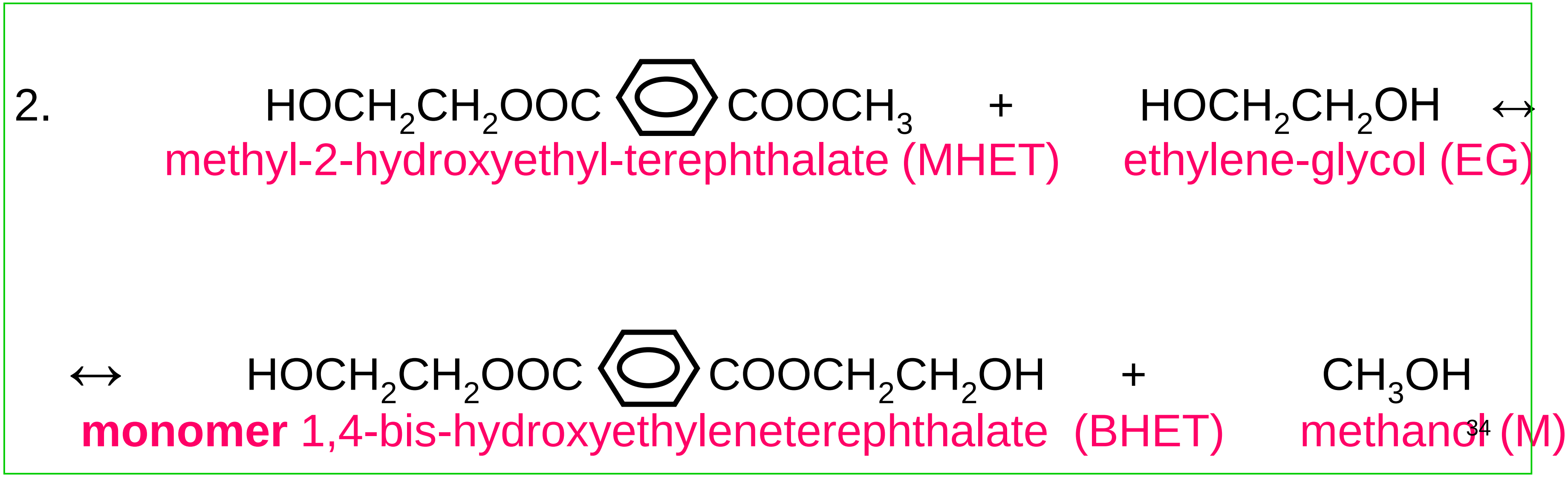
1. Direct esterification

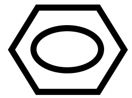


(The same reaction is in the previous slide.)

2. Ester exchange

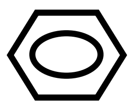




3. $HOCH_2CH_2OOC$  $COOCH_2CH_2OH$

monomer

1,4- 1,4-bis-hydroxyethyleneterephthalate (BHET)

$\leftrightarrow$ - [OOC-  $-COOCH_2CH_2]-$ + $HOCH_2CH_2OH$

ethylene-glycol (EG)

PET

2. ***One monomer with two types of functional groups:***

$$n\ H_2N\text{-}R\text{-}COOH \rightarrow [\ HN\text{-}R\text{-}CO\ ]_n\ + n\ H_2O$$

or generally:

$$\mathbf{n\ AB \rightarrow [\ A\text{-}B\ ]_n}$$

Example: polyamide

$$n\,H_2N\left(CH_2\right)_5COOH \rightarrow \left[\left(CH_2\right)_5CONH\right]_n + n\,H_2O$$

w-aminohexaacid nylon 6, perlon - polyamide

Reactions of polymerization are classified according to:

- mechanism of chain growth

- media of polymerization

Media of polymerization:

- homogeneous
- heterogeneous

2. Polymerizations
by the media of polymerization

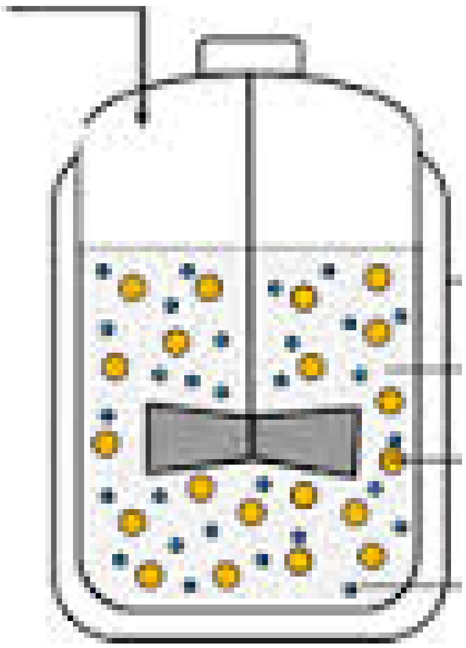
Polymerization processes –
in gas, liquid and solid phase
(depending on the medium)

Homogeneous polymerizations:

1. **Bulk polymerization**
2. **Solvent polymerization**

Heterogeneous polymerizations :

1. **Heterogeneous bulk polymerization**
2. **Heterogeneous solvent polymerization**
3. **Suspension polymerization**
4. **Emulsion polymerization**
5. **Polymerization in the gas phase**
6. **Interfacial polycondensations**



Homogeneous polymerizations

1. Bulk polymerization

- **monomer + initiator**
- there is **no solvent**
- only **one phase:**

  monomer and **polymer** are **compatible:**
  unreacted monomer acts as a solvent to polymer

Initiation - in monomeric phase usually with organic peroxides,
- initiators must be **completely soluble in monomer**

Limitations of bulk polymerization:

- **inefficient heat transfer -** high concentration of reactants -

- the control of reaction is not efficient

- high viscosity, mixing is difficult

- polymerization is not suitable for industrial processes

For industrial production

- it is necessary to control the chemical and thermal conditions of polymerization.

Example of self-initiated bulk polymerization:

polymerization of vinyl polymers –
long exposure to the sun (heat and UV light).

Obtained polymer – properties are not uniform
due to the uncontrolled conditions
of the polymerization reaction.

2. Solvent polymerization

- homogeneous polymerization
- **monomer + initiator + solvent**

- only one phase:

Monomer is soluble in solvent.

Polymer is also soluble in solvent.

- **solvent acts as diluent** in reaction mixture, reduces concentration of monomer

Solvent reduces concentration of reactants

- a decrease of reaction rate
- decrease of molecular weight

Solvent affects:

- molecular weight
- nature of the terminal groups of polymers

The most common solvents:
benzene, methanol, ethyl acetate…

Initiators: *substances for initiation of a polymerization* →
organic peroxides, often used:

dibenzoil peroxide, DBP

Advantage of solvent polymerization:

- very efficient heat transfer

  the heat developed during the reaction is distributed all over the system due to the presence of solvent and reduced concentration of the reactants

Disadvantages of solvent polymerization:

- low reaction rate *(low concentration of monomer)*
- obtaining low molecular weight polymer
- presence of solvent – solvent must be removed (evaporated) after polymerization

Heterogeneous polymerizations

1. Bulk polymerization

- **monomer + initiator**

- polymer is not soluble in monomer

- Monomer and polymer separate in reactor–
  two phases in reaction mixture
  – monomer and polymer layers are separated

- **Polymerization with precipitation**

2. Solvent polymerization

- **monomer + initiator + solvent**

- **monomer is soluble in solvent, polymer is not soluble in solvent –**
  two phases in reaction mixture

- **solvent provides good heat transfer**
- **Polymerization with precipitation**

Advantages:

- low viscosity
- efficient mixing